BUSINESS CONFIDENTIAL **PROJECT REPORT**

SUSPENSION VINYL RESINS:

THE INFLUENCE OF AN ANTIOXIDANT ON THE HEAT STABILITY OF PROCESS-12 RESIN

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SUMMARY An initial attempt has been made to improve the heat stability (ICMT) of Process-12 resin by the addition of an antioxidant to the resin. When as little as 40 ppm of butylated hydroxy toluene (BHT) was added to the resin, the ICMT (5 + 10 minutes) improved but the extended ICMT (15 and 20 minutes) did not improve. Therefore further effort to improve heat stability is needed.

Shelf-storage tests were run on Process-12 resin and revealed that the ICMT would decrease with time when the resin was stored in small paper bags in the laboratory. The rate of decline was significant and constant over the 3 to 4-month test period. The decline was not influenced by resin properties such as BHT concentration, type of catalyst used, and molecular weight of the resin. Other suspension resins may exhibit the same results. Shelf-storage tests are underway on Process-7 and Process-5 resins; preliminary results, at five weeks, suggest a similar decline in ICMT. Ordinary storage of Process-12 resin in sealed containers, such as fiber-pak drums, produced no decline in the ICMT property over a 4-month period.

More work should be done to define the mechanism of degradation and evaluate various possible solutions to the problem, such as use of linear CARBOWAX, evaluation of different antioxidants, and addition of buffers and other known heat-stability improvers, such as lauric acid.

INTRODUCTION Considerable effort has been expended at Texas City in the past year to develop a new suspension recipe, Process-12, which would produce a resin with good porosity, low fisheyes, low fines, good dry flow and good electrical properties. The suspending agent used for Process-12 is CARBOWAX 20M. One problem encountered in the development effort was with inadequate heat stability of the resin. Extensive evaluation of the heat stability of Process-12 resin was done by Mr. T. F. Hartsing at Bound Brook [2]. He concluded that the resins should not be offered for general sale to customers until the heat stability difficulties were resolved. In particular, he found that for soft, non-rigid systems (durometer A below 80), QXAM-12 resin was satisfactory and equal to QYTQ-7 resin; however, at higher durometer A values, the extended heat stability property became poorer than the QYTQ resin. Furthermore, for rigid PVC systems there is a basic stabilization interference of unknown type for QXAM-12 resin in both lead and tin mercaptide systems. Double-washing of the resin did not improve the stability of either system.

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As a consequence of Hartsing's work, a reevaluation of Process-12 resin was begun with the objective of seeking a method to improve the extended heat stability. The first approach to the problem was that which is reported in this study, the addition of the antioxidant BHT. This approach was chosen because of reported successful use of BHT (0.004% on a VCl basis) by the Kureha Chemical Industry Company of Japan [3], as well as normal use in Carbide's polyethylene. The mechanism proposed by the Japanese for the improvement in heat stability is that the antioxidant reacts with free radicals which are present at the termination of polymerization, and prevents oxidation during the resin recovery operation, which involves heating the resin.

Chemically, BHT is butylated hydroxy toluene and is also known as Ionol, 2,6-ditertiary-butyl-para-cresol (DBPC), and 4-hydroxy-3,5-di-tert-butyl-toluene [4].

CARBOWAX 20M is a high molecular weight polyethylene glycol made by coupling CARBOWAX 6M with the diglycidyl ether of bisphenol A. Dr. R. K. Barnes of the Technical Center in Charleston, West Virginia, reports [5] that CARBOWAX can air-oxidize like any ether to cleave the chain at the ether linkage and produce aldehyde products which are susceptible to more oxidation and color formation. The oxidation is base-catalyzed.

Several mechanisms are possible whereby the use of CARBOWAX could produce poor thermal stability of the resin: a) the CARBOWAX molecule may be incorporated into the PVC chain and subsequently break down on heating; b) the CARBOWAX may oxidize at either the ether linkage or at the coupling linkage and consequently initiate oxidization of the PVC. Possible beneficial modifications of CARBOWAX are a) use of a linear CARBOWAX 20M which contains no coupling agent, b) use of a different coupling agent, or c) addition of an antioxidant which will prevent oxidation, such as BHT (Ionol), Pana, Agerite Resin D, Agerite superlight [5].

The following section discusses the experiments in which various concentrations of BHT were added to several different Process-12 resins. Addition was made to the autoclave 10 minutes prior to termination. The dry resin samples, along with a control resin, were allowed to age in small brown paper bags at room temperature to determine the storage stability of the ICMT property.

DISCUSSION The following section discusses how these factors affect the ICMT property (heat stability) of Process-12 resin: addition of BHT antioxidant and influence of storage conditions; amount of BHT added; a cursory evaluation of suspending agent concentration, catalyst type, and molecular weight of the resin.

Effect of BHT Addition on the ICMT Property

The addition of BHT to an autoclave at the conclusion of the polymerization resulted in an increase in the initial value of the ICMT property by 5 to 10 units but did not improve the extended ICMT. See Figure 1 and Tables I and II for data on QXAM-12 and QXAP-12 results.

The manner in which the resin is stored after it is dried influences the stability of the ICMT rating with time. Samples were stored in small brown paper bags, in fiber-pak drums, and normal 50-lb. shipping bags and evaluated periodically to detect any change in ICMT property.

Resin stored in small paper bags and thereby given maximum exposure to air showed the most rapid decrease in ICMT value. An average for all samples evaluated showed a drop of 9 ±1 units per 30-day period without apparent decrease in the rate of drop over about a 90-day test period.

During the test period, resin was stored in ordinary fiber-pak drums. After about a 4-month period the drums were sampled and no change in the ICMT property was detected. See all Figures and Tables.

To get some idea if an ordinary 50-lb. shipping bag would protect the resin, a single bag of QXAM-12 resin (Blend 7) was obtained and evaluated after a storage period of 9 months, most of this time in an air-conditioned building. Probably because the bag had been standing on one end and thus air was present in the top and squeezed out of the bottom, a significant variation was found between the resin from the top and bottom. The top sample showed a drop in ICMT value of 10 to 20 units for a slow rate of 1 to 2 units per month. The bottom sample showed no change. The overall conclusion is that resin stored in the regular 50-lb. shipping bag would change only a small amount and then only when in contact with entrapped air or air entering from the bag-charging opening.

The above tests and observations indicate that Process-12 resin when exposed to atmospheric conditions will exhibit a steady rate of deterioration in ICMT property, whereas the same resin when stored in sealed containers showed no change. Presumably the deterioration results from oxidation.

Other suspension resins may also exhibit a decline in ICMT with time when evaluated by the same storage test. Preliminary results from a shelf-storage test show a possible aging trend (at 5 weeks) for both QSAN-7 and QYSA-5 resins (Figure 4); the tests will be continued for several months. Such a storage test is new to the author and was initiated when significantly different results were obtained when rechecking samples.

Effect of BHT Concentration on the ICMT Property

The amount of antioxidant to be added could be based, with some justification, on either the catalyst concentration, the CARBOWAX concentration, or the polymer produced. Any or all of these could influence the ICMT property of the resin. Residual catalyst, particularly free radicals, can cause decomposition of PVC polymer; CARBOWAX can oxidize and thereby trigger decomposition, and the polymer itself is known to undergo thermal decomposition in air by unzippering [6]. Therefore, all of the attached tables contain the amount of BHT added based on three factors: for catalyst, 1 to 130 per cent; for CARBOWAX, 0.4 to 8 per cent; and for PVC polymer, 0.004 to 0.04 per cent.

Examination of the data, particularly Figure 1 and Tables I and II, showed no apparent effect of BHT concentration variation on the ICMT property. It would appear that a minimum amount of antioxidant is required to react with some residual material and that any additional antioxidant serves no purpose. The author speculates that the BHT improves the initial ICMT value by reacting with residual free radicals from the peroxide catalyst and does not inhibit subsequent oxidation of the CARBOWAX, which causes a decrease in ICMT with time.

The amount of BHT which penetrated or adhered to the polymer particle may have been small because of the very low solubility of BHT in water. Upon addition of the BHT-isopropanol mix to water, the BHT would precipitate. A different antioxidant or a better way of getting the BHT onto the polymer might improve the effectiveness. Chemical analysis of the final resin should be used to establish the actual antioxidant concentration.

Effect of Various Factors on The ICMT Property

Two samples suggest the influence of CARBOWAX concentration on the ICMT property. Run 4-67-8, with 0.5 per cent, and Run 4-67-9, with 1.0 per cent CARBOWAX based on monomer charged, suggest that the increased amount of CARBOWAX decreased the initial ICMT rating by about 5 units but did not alter the rate of ICMT decline upon storage (Figure 1, Table II).

The shelf-storage stability of the ICMT rating was not altered by either the type of catalyst used to make the resin or the molecular weight of the resin. QXAP-12 resin, Table II and Table III, was made with IPP catalyst; QXAM-12 and QXAH-12 resins were made with DLP catalyst, Tables I and IV. Three different molecular weight resins showed essentially the same ICMT decline with aging (Figures 1, 2, 3); the approximate inherent viscosity level for QXAH was 0.78, for QXAM was 0.98, and for QXAP was 1.13.

Previous fundamental studies of Process-12 revealed the following with respect to the ICMT property [7,1]. The ICMT is definitely harmed by oxygen, increased polymerization temperatures, excess catalyst (DLP), excess CARBOWAX, IPP catalyst and oxygen (vs DLP and no oxygen) and sodium bicarbonate (the oxidization of CARBOWAX is base catalyzed; soda addition keeps the polymerization charge basic and without soda the system becomes acid). The ICMT property is helped by low polymerization temperatures and therefore the QYSL grade (QSAS) should have the best properties. Previous work [7] suggests that the following may be helpful to the ICMT property: use of DLP catalyst (vs IPP), a charge-water temperature of 45°C (vs 25°C), and a monomer/water ratio of 30/70 (vs 35/65). The latter two conditions may influence the "washing" action. Washing is known to be helpful when some ingredient like soda is present and needs to be removed.

Proposed Study of Factors Which May Improve the ICMT Property

The following suggestions are proposed for further work to improve the heat stability of Process-12 resin.

Tests should be performed to better-define the mechanism of degradation and thereby assist in finding a solution to the heat stability problem. Storage of resin in oxygen-free, clear bottles should indicate if oxygen is the primary factor or if light also contributes to the change in ICMT value with time. A thorough washing of resin with various solvents to remove all materials except polymer should permit an evaluation to be made of the stability of the polymer chain. Evaluation of a linear CARBOWAX 20M should determine if the coupling agent in the standard CARBOWAX 20M is the bad actor. If the results are bad then the coupling agent is not to blame, but if good, then the solution is to use either linear CARBOWAX or find a different coupling agent. Evaluation of different antioxidants should be made to try and find a material which will better penetrate and adhere to

the polymer. Dissolving the antioxidant in melted CARBOWAX should be considered. Analysis of the amount of antioxidant actually present on the resin is recommended; this was not done in the present study. Addition of known stabilizers, such as lauric acid, to the polymer should be evaluated.

CONCLUSIONS AND RECOMMENDATIONS

1. The addition of BHT to Process-12 resin improved the ICMT reading (5 + 10 min) but did not help the extended ICMT (15 and 20 min). The presence of BHT did not prevent a drop in ICMT with time during a shelf-storage test.

2. The improvement in ICMT from BHT addition is not a function of the amount added; an excess over the minimum amount needed does not give any further improvement.

3. Future effort is needed to better define the mechanism of degradation and to find a solution to the problem. The following should be tested: linear CARBOWAX, different antioxidants, buffers, and complete washing of the resin.

4. Shelf-storage tests were run in which resin was stored in small paper bags in the laboratory. Over a 4-month period, Process-12 resin exhibited a steady and significant decline in ICMT (9 ±1 units per month). Other suspension resins may exhibit the same trend; preliminary results (at 5 weeks) from a storage-stability test for QSAN-7 and QYSA-5 resin show a possible downward trend similar to the Process-12 resin. These tests are continuing.

5. Storage in a closed container such as a fiber-pak drum or a 50-lb. bag prevented any significant drop in ICMT during a 4-month period.

EXPERIMENTAL BHT was added to the autoclave at the normal termination point and the contents allowed to agitate for an additional 10 minutes. The BHT was added as an isopropanol solution (155 grams of BHT in one gallon of isopropanol).

Two methods were used to evaluate the influence of BHT addition: a) determination of the ICMT value of the resin immediately after production, and b) storage stability of the resin. Immediately after production, about 3 to 5 pounds of resin were placed in each of many ordinary brown paper bags and stored on the shelf in an air-conditioned laboratory. At various time intervals a bag would be removed and the ICMT property determined. During the storage period, resin was stored in ordinary 40-gallon fiber-pak drums. At the conclusion of the paper-bag storage test, a sample was removed from the previously-unopened drum and an ICMT test run for a storage-condition comparison.

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T. R. Smith

Attachments: Five Tables
Four Figures

TABLE I

QXAM-12 RESIN
INFLUENCE OF ANTIOXIDANT ON HEAT STABILITY

Run No.	Date	Elapsed Time days (2)	ICMT TEST (1) ICMT 5+10	Readings 5	10	15	20	Antioxidant Addition Wt. % BHT (3) based on Cat. (4)	based on C20M (4)	based on VCl	Remarks
3-67-20	3-29	0	94	47	47	44	24	0	0	0	Control Run
	4-1	3	88	44	44	44	25				
	4-4	6	90	44	46	39	10				
	4-11	13	85	44	41	42	14				
	4-21	23	87	43	44	38	11				
	5-11	43	80	40	40	35	8				
	6-1	64	81	41	40	29	7				
	7-14	107	61	30	31	25	-				
	7-20	113(5)	98	52	46	10					
3-67-21	3-30	0	105	53	52	29		1.34	0.40	0.004	
	4-1	2	100	49	51	14					
	4-4	5	100	49	51	14					
	4-11	12	98	47	51	13					
	4-21	22	97	48	49	13					
	5-11	42	91	45	46	9					
	6-1	64	85	43	42	10					
	7-14	107	64	32	32	-					
	7-20	113(5)	109	56	53	20					

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(1) UCC Method WC-163-C
(2) Time since sample was dried. Resin immediately placed in small brown paper bags for storage in air-conditioned lab.
(3) BHT = butylated hydroxy toluene (Ionol). Added to autoclave at end of polymerization.
(4) Cat. = DLP; C2OM = CARBOWAX at 1.0% based on VCl.
(5) Resin stored in full 40-gallon fiber-pak drum.

TABLE II

QXAP-12 RESIN: PILOT PLANT SAMPLES
INFLUENCE OF ANTIOXIDANT ON HEAT STABILITY

Run No.	Date	Elapsed Time days(2)	ICMT TEST (1) ICMT 5+10	Readings 5	10	15	20	Antioxidant Addition Wt. % BHT (3) based on Cat. (4)	based on C20M (4)	based on VCl	Remarks
4-67-8	4-13	1	105	53	52	42	6	0	0	0	Control Run; 1/2% C20M
(5)	4-17	5	103	51	52	46	8				
	4-26	14	105	52	53	48	14				
	5-31	49	88	44	44	37	11				
	7-20	99(6)	106	52	54	51	28				
4-67-8BHT	4-13	1	108	54	54	44	7	134.	8	0.04	1/2% C20M
(5)	4-14	5	106	52	54	46	9				
	4-26	14	108	55	53	46	10				
	5-31	49	97	49	48	41	10				
4-67-9	4-13	0	104	52	52	44	7	134	4	0.04	1% C20M
	4-17	4	106	52	54	42	6				
	4-26	13	100	50	50	44	8				
	5-11	28	96	48	48	39	8				
	6-28	77	83	42	41	36	7				
	7-20	99(6)	108	54	54	50	24				

(1) UCC Method WC-160-C.
(2) Time since sample was dried. Resin immediately placed in small brown bags and stored in air-conditioned lab.
(3) BHT = butylated hydroxy toluene (IONOL). Added to autoclave at end of polymerization.
(4) Cat. = IPP; C20M = CARBOWAX C20M.
(5) Run 8 and *BHT represent respectively resin removed from autoclave immediately before and after BHT additions.
(6) Resin stored in full 40-gallon fiber-pak drum.

TABLE III

QXAP-12 RESIN: PRODUCTION SAMPLES
INFLUENCE OF ANTIOXIDANT ON HEAT STABILITY

Run No.	Date	Elapsed Time since produced, days	Elapsed Time stored in small bags(2) days	ICMT TEST (1) ICMT 5+10	Readings 5	10	15	20	Antioxidant Addition Wt. % BHT (3) based on Cat. (4)	based on C20M (4)	based on VCl
Bin 608	4-22	0	0	103	50	53	51	47	105.	8.1	0.04
(5)	4-25	3	3	106	52	54	51	42			
	5-11	19	19	101	49	52	46	35			
	6-01	40	40	89	44	45	41	16			
	6-02	41	41	79	38	41	38	21			
	6-22	61	61	88	42	46	43	29			
	7-20	89	(8)	108(8)	53	55	54	43			
Blend No. 1	6-02(6)	41	0	105	52	53	47	22	105.	8.1	0.04
(6)	6-23	62	21	94	46	48	43	23			
	7-07	76	35	92	44	48	44	31			
	7-07	76	(7)	105(7)	52	53	48	33			
	7-25	94	53	95	47	48	43	24			
	8-01	101	60	79	38	41	38	17			
	8-08	108	67	86	42	44	42	23			

(1) UCC Method WC-160-C
(2) Resin placed in small brown paper bags and stored on the shelf in an air-conditioned lab.
(3) BHT = butylated hydroxy toluene (IONOL). Added to autoclave at end of polymerization.
(4) Cat. = IPP; C20M = CARBOWAX, 0.5% based on VCl charge.
(5) Spot sample from Blend No. 1.
(6) A 50-lb. bag was shipped to Tarrytown, N. Y., then returned in a fiber drum to Texas City for testing.
(7) Resampled fiber drum from Blend No. 1(6) to compare with samples stored in bags.
(8) Resin stored in a 3/4-full 40-gallon fiber-pak drum.

TABLE IV

QXAH-12 RESIN

INFLUENCE OF ANTIOXIDANT ON HEAT STABILITY

Run No.	Date	Elapsed Time Days (2)	ICMT TEST (1) ICMT 5 + 10	Readings 5	10	15	Antioxidant Addition Wt. % BHT (3) Based On Cat. (4) 40.	Based On C20M (4) 6.7	Based On VCl 0.04
4-67-13	4-20	1	101	53	48	6			
	4-24	5	98	51	47	6			
	5-05	16	95	50	45	6			
	5-17	28	91	47	44	5			
	5-31	42	94	47	47	14			
	6-28	70	69	35	34	6			
	6-29	71	75	40	35	5			
	7-20	92(5)	102	56	46	4			

(1) UCC Method WC-163-C
(2) Time since sample was dried. Resin immediately placed in small brown paper bags for storage in air-conditioned lab.
(3) BHT = butylated hydroxy toluene (IONOL). Added to autoclave at end of polymerization
(4) Cat. = DLP; C20M = CARBOWAX, 0.6% based on VCl charge
(5) Resin stored in 3/4-full 40-gal fiber-pak drum

TABLE V

QXAM-12 RESIN BLEND NO. 7 (1)
STORAGE TEST: 50-LB BAG

Date	Elapsed Time Since Resin was Produced	ICMT TEST (2) READINGS					Remarks
		5 + 10	5	10	15	20	
	Months						
October 11, 1966	0	103	51	52	35	10	Original Blend Analysis
July 25, 1967	9-1/2	93	46	47	28	-	Bag Opened, Sampled From Top
August 1, 1967	9-3/4	83	41	42	11	-	Resampled From Top
August 8, 1967	10	102	50	52	32	6	Sampled From Bottom

(1) This resin contained no BHT antioxident. The 50-lb bag was stored unopened in an air-conditioned building during the test period.

(2) UCC Method WC-163-C

FIGURE 1

EFFECT OF AGING ON HEAT STABILITY

QXAM-12 AND QXAP-12 RESINS

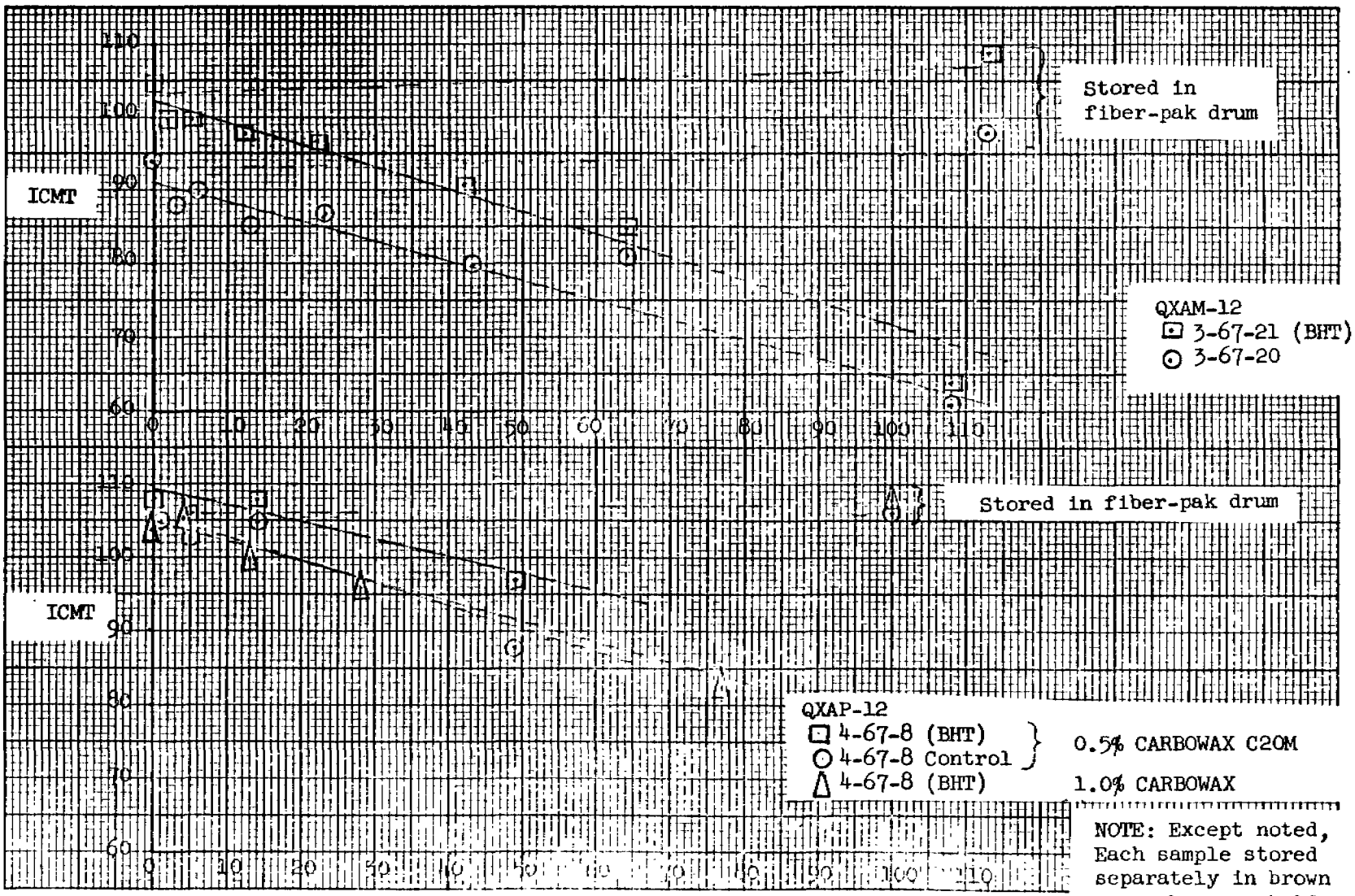
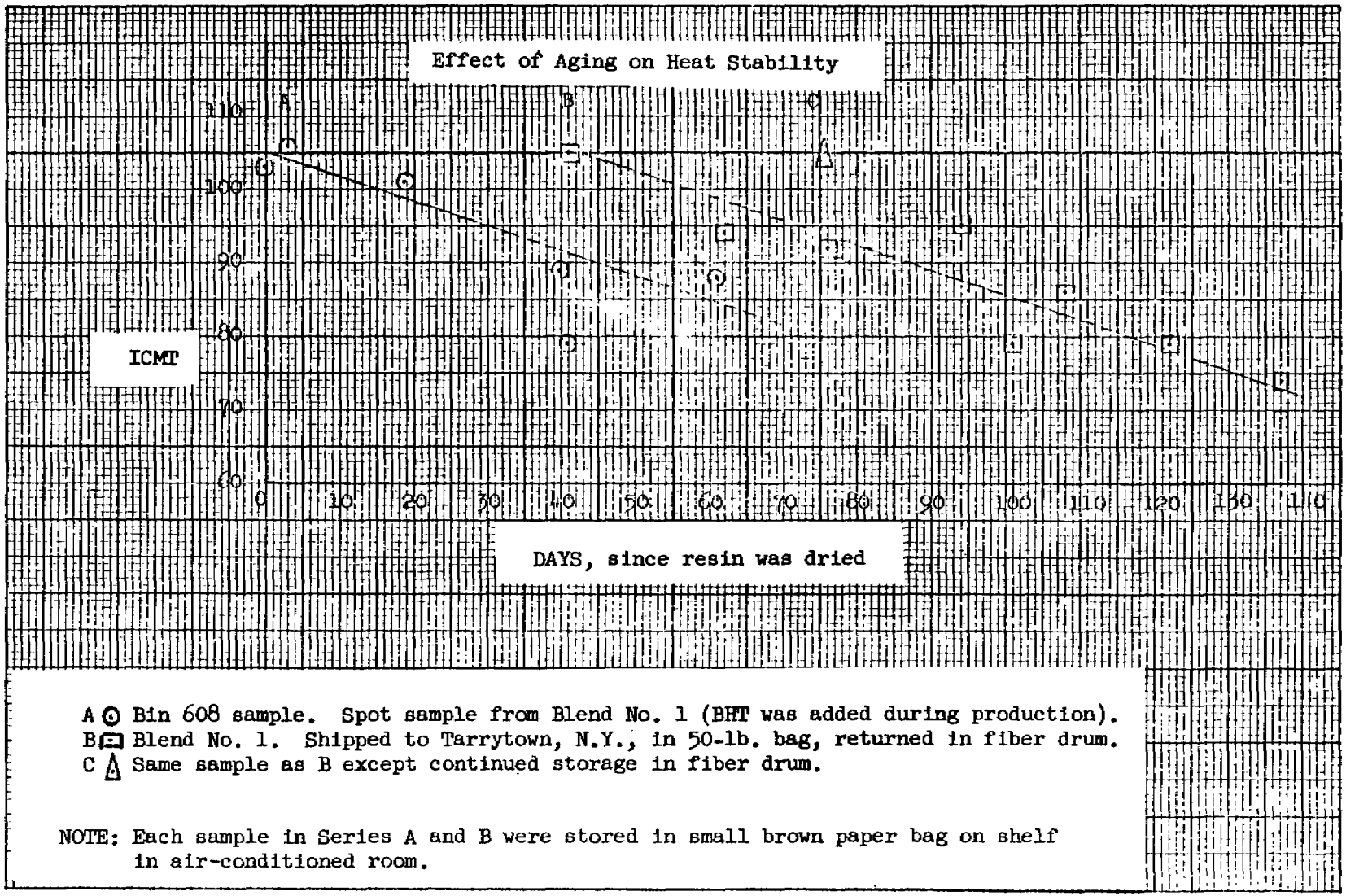


FIGURE 2

QXAP-12 RESIN:

PRODUCTION RUN



A ⊙ Bin 608 sample. Spot sample from Blend No. 1 (BHT was added during production).
B ▭ Blend No. 1. Shipped to Tarrytown, N.Y., in 50-lb. bag, returned in fiber drum.
C △ Same sample as B except continued storage in fiber drum.

NOTE: Each sample in Series A and B were stored in small brown paper bag on shelf in air-conditioned room.

FIGURE 3

QXAH-12 RESIN

EFFECT OF AGING ON HEAT STABILITY

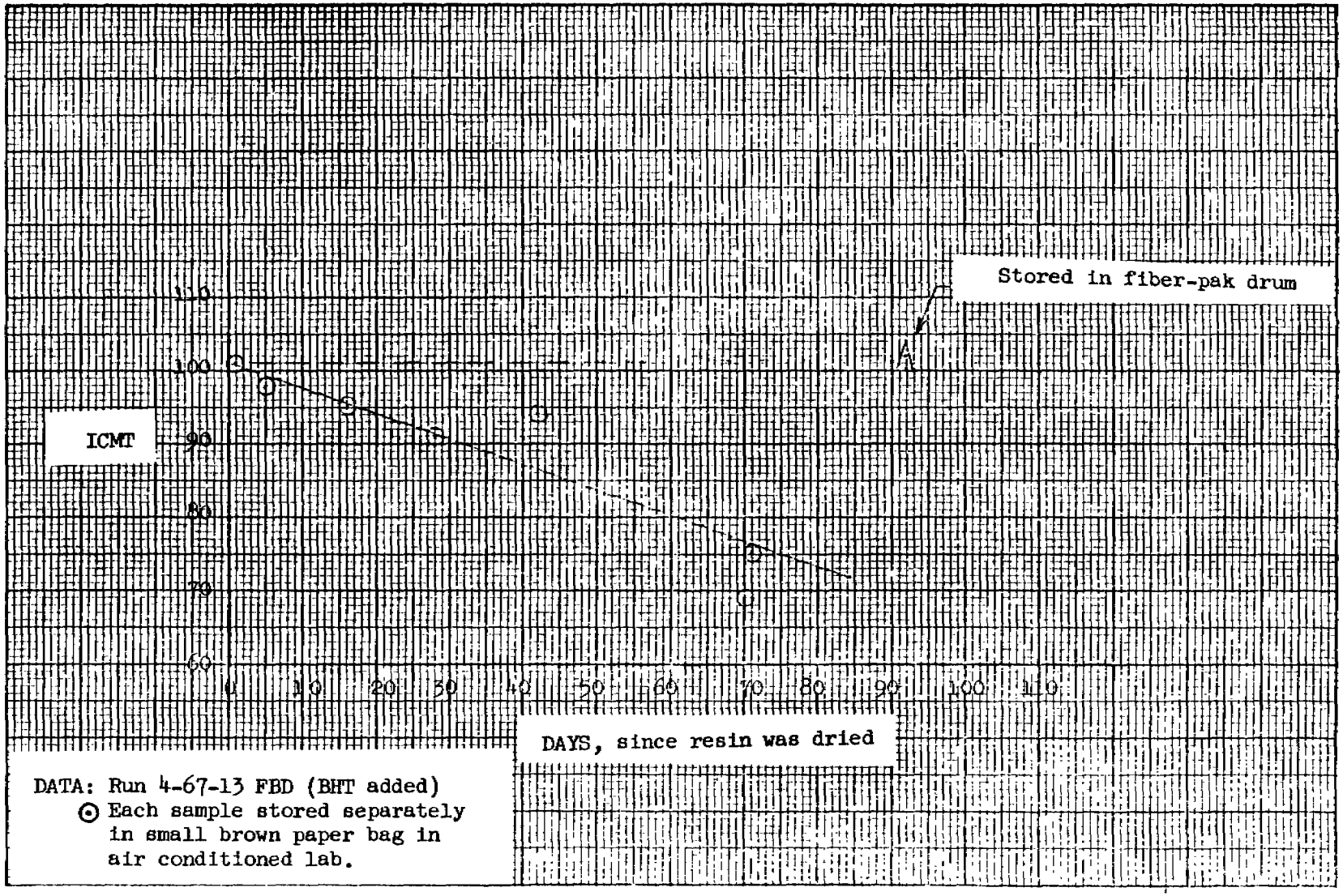


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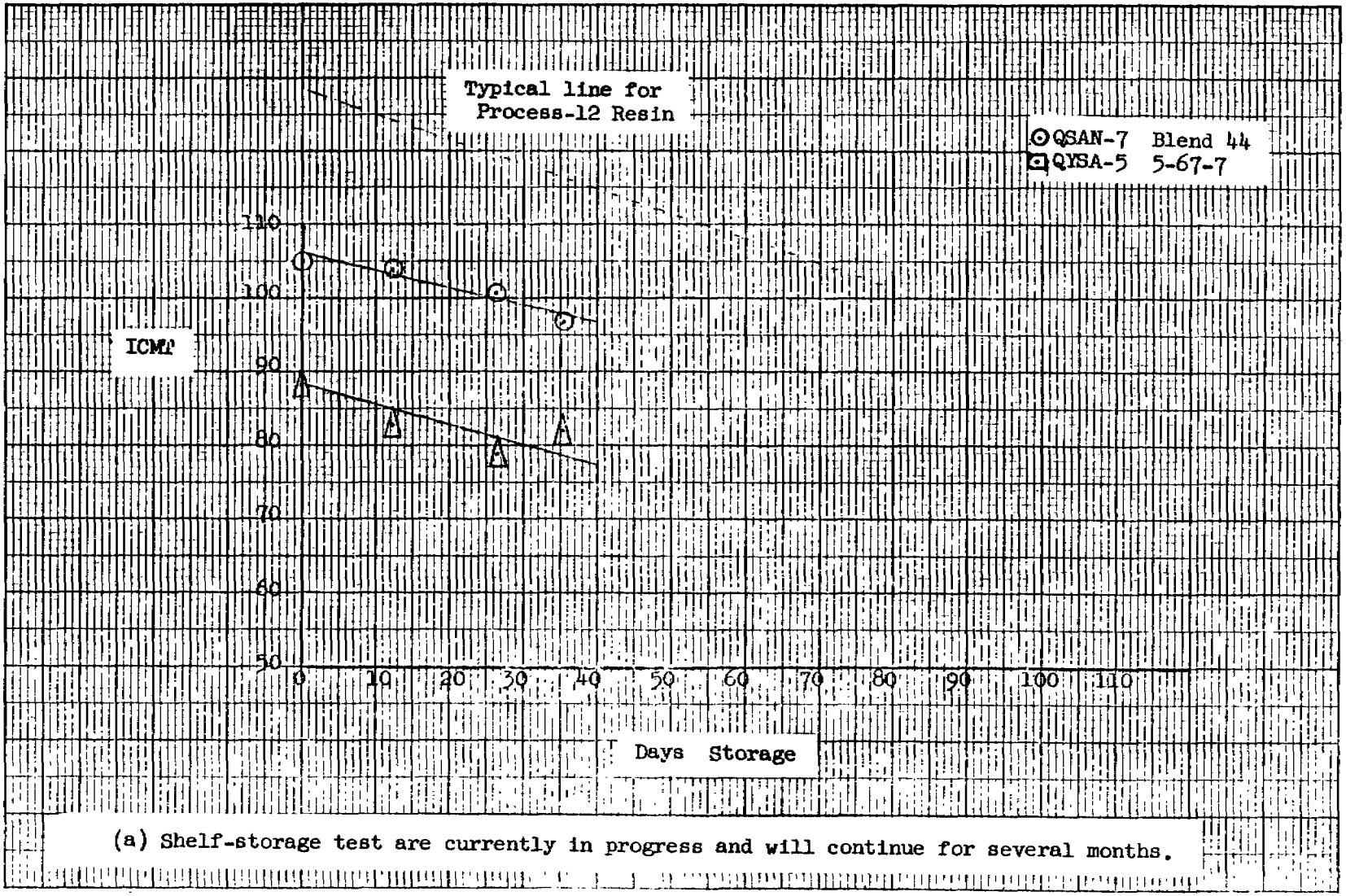
FIGURE 4

EFFECT OF AGING ON HEAT STABILITY: PRELIMINARY RESULTS (a)

QSAN-7 AND QYSA-5 RESINS



(a) Shelf-storage test are currently in progress and will continue for several months.

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